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II.

SCHEELE'S GREEN,

ITS COMPOSITION AS USUALLY PREPARED, AND SOME EXPERIMENTS UPON ARSENITE OF COPPER.

BY S. P. SHARPLES, S.B.

Presented, June 14, 1876.

IN 1778, the eminent Swedish chemist, Charles William Scheele, communicated to the Academy of Sciences at Stockholm the method of preparing the green pigment which has since borne his name. He, however, says, that it was discovered three years previously.

This pigment is of a yellowish green color, and has been long used in the arts under various names; such as, mountain green, mineral green, and Swedish green. At the time of its discovery, it was the most brilliant green obtainable.

The discovery, in 1814, of the copper aceto-arsenite, known as Schweinfurth green, Paris green, English green, and sometimes wrongly called Scheele's green, has, however, almost entirely thrown Scheele's green out of the market; and it is at the present day an unknown substance, so far as its use as a pigment is concerned; although it may be still found on the price lists of manufacturing chemists, and the receipts for its manufacture are found in works on dyeing and calico-printing. But its covering power is very low, and it is far inferior in brilliancy to its successful rival, Paris green.

Having had occasion to examine some samples of this pigment some time ago, I became convinced that the composition of Scheele's green, as laid down in the books, was altogether a matter of conjecture; since I could find no record of any analysis that had ever been made of the substance prepared according to Scheele's directions, which have been copied without change for the last hundred years.

The formula given varies with the date; Scheele himself, of course, neither made a quantitative analysis nor gave a formula. Succeeding writers seem to have followed him in the first respect, but have given formulas to correspond with their ideas of the composition that the salt should have.

The older writers give the formula CuOAs_2O_3 , this would give the percentages of copper oxide and arsenic trioxide, as follows:—

Copper oxide,	29.50
Arsenic trioxide,	70.50
	<hr/>
	100.00

(The atomic weights used through this paper are: oxygen, 16; copper, 63.4; the old formulas being changed to correspond to these weights. As a matter of convenience, I have made all statements of composition in terms of copper oxide and arsenic trioxide, but in so doing I have no wish to be understood as asserting that they exist as copper oxide and arsenic trioxide in the compound.)

Berzelius* gives the formula, Cu_2As ; this, in modern notation, would be $\text{Cu}_2\text{As}_2\text{O}_5$; or in percentages,

Copper oxide,	44.50
Arsenic trioxide,	55.50
	<hr/>
	100.00

He describes the methods by which it may be obtained as either, by digesting carbonate of copper with water and arsenious acid, or by Scheele's method, giving for the latter almost exactly Scheele's receipt.

Ure† gives Scheele's receipt, and then says it consists of oxide of copper, 28.51, arsenious acid, 71.46. This corresponds to the first formula given above, CuAs_2O_4 .

Miller‡ gives the formula CuHAsO_3 . This in percentages would be:

Copper oxide,	42.37
Arsenic trioxide,	52.83
Water,	4.80

This formula seems to be the favorite one at present, and may be found in most of the text-books.

Bloxam,§ in the course of his long and elaborate investigations of the arsenites, made some experiments upon copper arsenite, but failed to obtain a definite compound. The first salt made, he says, contained:—

* Ure's Dict., New York, 1847, p. 1100.

† Traité de Chimie, Tome 4, p. 182. Paris, 1847.

‡ Miller's Elements of Chemistry. London, 1864, p. 292.

§ Bloxam, C. L., Jour. Chem. Soc., 1862, p. 292.

	Per cents.	Equivalents.
Copper oxide,	40.54	1.88
Arsenic trioxide,	53.80	1.
Water,	5.67	1.16

The second contained :—

	Per cents.	Equivalents.
Copper oxide,	44.29	2.21
Arsenic trioxide,	49.98	1.00
Water,	5.73	1.26

The third product gave :—

	Per cents.	Equivalents.
Copper oxide,	46.52	2.35
Arsenic trioxide,	49.36	1.00
Water,	4.12	.92

The fourth gave :—

	Per cents.	Equivalents.
Copper oxide,	42.69	1.96
Arsenic trioxide,	52.67	1.
Water,	4.64	.97

From this last analysis he deduces the formula CuHAsO_3 . In a foot-note he says: "Scheele's prescription for the commercial green arsenite of copper involves 2.3 equivalents of oxide of copper for one equivalent of arsenious acid, so that Scheele's green dried at 212°F. , appears to be essentially a mixture of CuHAsO_3 , with an excess of oxide of copper."

This observation is perfectly correct if nothing is taken into the account except the quantities taken by Scheele; but Scheele himself says, in a foot-note: * "The water with which the color is lixiviated contains a little arsenic, and must not be thrown out in a place to which cattle have access." The evident tendency of this loss of arsenic would be to make the salt more basic than the formula $(\text{CuO})_{2.32}\text{As}_2\text{O}_3(\text{H}_2\text{O})_{92}$ calls for, this being the formula which Bloxam supposes to represent Scheele's green.

In Watts's Dictionary,† under the head of arsenite of copper, this sentence occurs: "It is a light green precipitate, which dissolves in an excess of ammonia, without color, yielding a solution of arsenic acid and cuprous oxide."

Berzelius's formula is given, and the sentence just quoted is evi-

* Scheele's Essays. London, 1786, p. 254.

† Vol. I., p. 376.

dently a translation, either directly or indirectly, from the same author.

The description of copper arsenite in the French edition of Berzelius, Paris, 1847, is as follows: "The neutral salt is obtained by precipitating sulphate of copper by arsenite of potassa. The precipitate is green. When it contains an excess of base, its color is more intense; but it decomposes spontaneously, in a little time becoming a dark brown, and then contains cupric arsenate and cuprous arsenite. Caustic ammonia dissolves this salt into a colorless liquid containing, probably, cuprous arsenate." The German of 1838 is the same as the above, with the exception that it reads: "When the alkali is in excess, the color is more intense, but it decomposes in a little time," &c. "This salt" referred to in the above paragraph, is evidently the brown salt, and not the green. Moreover, the German text, and not the French, is the correct one, as is shown by my own experiments.

In this connection, the following extract is of interest. Rose says of Scheele's green: "This precipitate is soluble in an excess of ammonia, also in an excess of hydrate of potassa. The solution has in both cases a similar blue color. The blue solution formed by hydrate of potassa deposits in time reddish-brown suboxide of copper; the liquid becomes colorless, and contains arsenate of potassium. The blue solution formed by ammonia is not modified by time."

The reference from Berzelius seems to have been misunderstood by German as well as English writers, as the same statement occurs in the *Handwörterbuch der Chemie*, B. 2, 1858, p. 300, which says Scheele's green dissolves colorless in ammonia as arsenic acid and cuprous oxide. Graham-Otto* also repeats the same.

In the *New Chemistry*,† the above blunder is repeated, and two formulas are given, as follows: "Arsenite of copper, $(\text{Cu}_2\text{O})_2\text{As}_2\text{O}_3$ or, $\text{Cu}_3(\text{AsO}_3)_2$." And the article finishes by saying there are also two hydrated salts, $\text{CuH}_4(\text{AsO}_3)_2$, and CuHAsO_3 . The percentage composition of these salts would be as follows, supposing the above formulas are correctly given:—

	$(\text{Cu}_2\text{O})_2\text{As}_2\text{O}_3$.	$\text{Cu}_3(\text{AsO}_3)_2$.	$\text{CuH}_4(\text{AsO}_3)_2$.	CuHAsO_3 .
Copper oxide, (sub. 59.06)		54.61	25.33	42.37
Arsenic trioxide,	40.94	45.39	63.18	52.83
Water,			11.49	4.80

* Vol. III., 557, 4th ed.

† Chemistry, Theoretical and Practical. Lippincott & Co.; Phila., 1876, p. 260.

In the first of these formulas, there is an evident mistake; it is a copy of the formula given by Watts, without taking into account that Watts, while doubling the atomic weight of oxygen, retained the old weight of copper, so that, corrected, this formula reads $(\text{CuO})_2 \text{As}_2\text{O}_3$; or, in other words, is Berzelius's formula.

But both of the formulas, one and two, are wrong, from the fact that they contain no water. No. 3 is an evident attempt to represent the acid arsenite which Berzelius mentions, and No. 4 is Bloxam's formula.

As will be seen, the whole literature of the subject is founded upon three sets of facts. Scheele's prescription, which all the authors, whom I have quoted, have given, making only such alterations as were necessary on account of changes in weights and measures. And it is a singular fact, that not one of these authors has taken the trouble to see if the quantities of copper sulphate and arsenic trioxide taken would produce a salt of the formula given; or have discovered the fact that nearly twice as much potassium carbonate is used as is necessary to saturate the sulphuric trioxide of the copper sulphate, and Scheele's foot-note has been totally ignored.

Secondly, Berzelius's account of the salt, which has evidently been misunderstood.

Thirdly, Bloxam's analyses of salts, which he would have found difficult, if not impossible, to reproduce, had he been so inclined.

After comparing the various works cited, it became a matter of interest to find out, in the first place, what Scheele's green really is, what are its properties, and whether there is more than one copper arsenite.

The experiment was tried of making copper arsenite according to the method given by Berzelius; that is, by dissolving copper carbonate in an aqueous solution of arsenic trioxide.

Hydrocopper carbonate was prepared by precipitating copper sulphate in the cold by an excess of sodium carbonate, and washing the precipitate with cold water until free from sulphates. Some of the precipitate was boiled with a saturated solution of arsenic trioxide, its blue color soon changed to a bright green, which it maintained, although boiled for upwards of an hour. The green precipitate was filtered off, and washed with hot water, until the wash waters were free from arsenic.

The substance remaining on the filter was of a bright green color, scarcely inferior to Schweinfurth green in brilliancy, although of a yellowish shade.

The green precipitate was dried and analyzed, it gave,—

ANALYSIS No. I.

	Per cents.	Atomic Ratios.
Copper oxide,	66.02	8.31
Arsenic trioxide,	8.32	.42
Carbon dioxide,	15.26	3.47
Water,	10.33	5.74
	<hr/> 99.93	

This corresponds well with a mixture of dibasic carbonate and tribasic arsenite.

The brown basic carbonate produced by boiling the hydrocopper carbonate with water was then boiled with arsenic trioxide, but was not changed in color. The filtrate from the green precipitate contained a large amount of arsenic, but was free from copper; and I failed to obtain on evaporation the yellowish-green acid salt spoken of by Berzelius.

Further experiments on the carbonate were tried to see if it could be completely decomposed by boiling with excess of arsenic trioxide, but they all resulted in failure.

It seems to me that Berzelius must have been misled by the production of the brilliant green arsenio-carbonate, as he gives no analysis to support his assertion.

Arsenic trioxide seems to have a very strong influence in preventing the blackening of copper carbonates and hydrates, a very small percentage preventing this well-known reaction.

A series of experiments were then tried on the production of Scheele's green, following the course laid down in the books and by Scheele himself; viz., first, the production of a more or less basic, sodium or potassium arsenite; and, secondly, the addition of this to a solution of copper sulphate.

Experiment No. 1.

		Parts.	Atomic Ratios.
Copper sulphate,	$\text{CuSO}_4\cdot 5\text{H}_2\text{O}$	50	2.04
Potassium carbonate,	K_2CO_3	25	1.81
Arsenic trioxide,	As_2O_3	10	.50

Dissolved the potassium carbonate in water, boiled and added the arsenic trioxide, filtered and added to the boiling solution of copper sulphate. The precipitate, when washed and dried, was of a yellowish green; the filtrate was blue.

ANALYSIS No. II.

	Per cents.	Atomic Ratios.
Copper oxide,	56.98	7.18
Arsenic trioxide,	21.45	1.08
Sulphur trioxide,	12.80	1.60
Ferrous oxide,	1.60	.22
Water,	7.17	3.98

Experiment No. 2.

		Parts.	Atomic Ratios.
Copper sulphate,	$\text{CuSO}_4\cdot 5\text{H}_2\text{O}$	50	2.04
Potassium carbonate,	K_2CO_3	30	2.17
Arsenic trioxide,	As_2O_3	15	.76

Treated as before; filtrate pale blue, precipitate, a brighter green than No. 1.

ANALYSIS No. III.

	Per cents.	Atomic Ratios.
Copper oxide,	49.58	6.24
Arsenic trioxide,	32.12	1.62
Sulphur trioxide,	4.42	.55
Water,	13.88	7.82

Experiment No. 3.

		Atomic Ratios.
$\text{CuSO}_4\cdot 5\text{H}_2\text{O}$,	50	2.04
K_2CO_3 ,	40	2.90
As_2O_3 ,	10	.50

Treated as before; filtrate pale yellow, precipitate had more of a yellowish tinge than before.

ANALYSIS No. IV.

	Per cents.	Atomic Ratios.
Copper oxide,	51.26	6.43
Arsenic trioxide,	31.67	1.60
Sulphur trioxide,	5.32	.66
Water,	11.75	6.53

Experiment No. 4.

	Parts.	Atomic Ratios.
$\text{CuSO}_4\cdot 5\text{H}_2\text{O}$,	50	2.04
K_2CO_3 ,	50	3.61
As_2O_3 ,	18	.90

The potash and arsenic were dissolved and allowed to cool, then added to the cold solution of copper. The mixture effervesced strongly; half of it was allowed to stand until next day, then filtered; the other half was boiled, which operation it stood without blackening. Analysis of the first half gave, —

ANALYSIS No. V.

	Per cents.	Atomic Ratios.
Copper oxide,	49.55	6.24
Arsenic trioxide,	38.90	1.96
Water,	11.55	6.42

The second half gave, —

ANALYSIS No. VI.

	Per cents.	Atomic Ratios.
Copper oxide,	46.65	5.87
Arsenic trioxide,	42.94	2.17
Water,	10.41	5.78

This preparation was repeated, using the same proportions; the precipitate was boiled, and washed with hot water until the filtrate was free from arsenic.

ANALYSIS No. VII.

	Per cents.	Atomic Ratios.
Copper oxide,	51.40	6.47
Arsenic trioxide,	39.57	1.99
Water,	8.72	4.85

This seems to indicate that either the salt is decomposed by washing with hot water, or that it consists of a strongly basic salt mixed with free arsenious acid. The first view is most likely the correct one, if we modify it so as to read: "it is decomposed by washing with either hot or cold water, forming a more basic salt."

But further experiments seem to show that this decomposition is much slower with cold than with hot water. And I have found it utterly impossible to remove the whole of the arsenic by prolonged washing.

This fact was further confirmed by an experiment of Prof. J. M. Ordway, who washed a portion of the salt with 3,000 times its weight of water, without completely decomposing it. The basic salt produced by washing does not blacken on boiling with water, thus showing that we have a true basic salt or mixtures of several basic salts, and not a mixture of Bloxam's normal arsenite, HCuAsO_4 , and hydrate of copper.

Experiment No. 5.

In order to see if the salt HCuAsO_4 could be prepared by taking the exact amount of arsenic trioxide and copper sulphate necessary to form it, the following proportions were taken : —

	Parts.	Atomic Ratios.
Copper sulphate,	124.8	2.
Arsenic trioxide,	49.5	1.
Sodium carbonate,	53.	2.

The solution of arsenic in the sodium carbonate was boiled, and added, while boiling, to the solution of copper sulphate. And the ebullition was continued till all the carbonic acid was driven off. The precipitate was washed by decantation once or twice, and then divided into three portions; the first was merely drained, the second was washed a little, and the third was washed until arsenic ceased to be found in the wash-water. These portions were numbered respectively, VIII., IX., X. They all contained basic copper sulphate, and No. VIII. probably contained a little sodium sulphate.

ANALYSIS No. VIII.

	Per cents.	Atomic Ratios.
Copper oxide,	49.78	6.27
Arsenic trioxide,	35.93	1.80
Sulphur trioxide,	6.07	.76
Water,	7.56	4.20
	<hr/> 99.34	

ANALYSIS No. IX.

	Per cents.	Atomic Ratios.
Copper oxide,	47.71	6.00
Arsenic oxide,	43.74	2.21
Sulphur trioxide,	3.10	.39
Water,	5.47	3.04
	<hr/> 100.02	

ANALYSIS No. X.

	Per cents.	Atomic Ratios.
Copper oxide,	57.77	7.27
Arsenic oxide,	27.50	1.39
Sulphur trioxide,	5.27	.66
Water,	8.97	4.98
	<hr/> 99.51	

None of the above blackened on boiling with water, and all gave a blue solution with ammonia. Nos. VIII., IX. closely approximate a mixture of tribasic sulphate with Bloxam's salt; while No. X. is more basic than the formula for triarsenite calls for.

Experiment No. 6.

	Molecules.
Copper sulphate,	6
Sodic carbonate,	3
Arsenic trioxide,	1

The filtrate was blue and acid; the precipitate gave, —

ANALYSIS No. XI.

	Per cents.	Atomic Ratios.
Copper oxide,	60.80	7.66
Arsenic trioxide,	14.53	.73
Sulphur trioxide,	13.34	1.67
Water,	11.11	6.17

This corresponds with a mixture of tribasic arsenite and sulphate, with a little excess of copper oxide.

To the blue filtrate from the above, three molecules more of sodic carbonate were added, the filtrate was faint yellow, and free from copper, but contained arsenic; the precipitate contained a little carbonate.

ANALYSIS No. XII.

	Per cents.	Atomic Ratios.
Copper oxide,	56.71	7.14
Arsenic trioxide,	28.62	1.44
Sulphur trioxide,	1.59	.20
Water,	9.50	5.28
Carbon dioxide,	3.35	.77
	<hr/> 99.77	

These precipitates both dissolved in ammonia with a blue color, and stood boiling without change of color.

Experiment No. 7.

	Molecules.
Copper sulphate,	6
Potassium carbonate,	6
Arsenic trioxide,	1

Boiled for half an hour, filtrate colorless, free from copper, but contained arsenic; precipitate did not blacken on boiling, was free from carbonates, but contained basic sulphate. Washed until filtrate was free from arsenic.

ANALYSIS No. XIII.

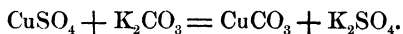
	Per cents.	Atomic Ratios.
Copper oxide,	58.85	7.41
Arsenic trioxide,	27.08	1.37
Sulphur trioxide,	4.83	.60
Water,	8.55	4.75
	<hr/> 99.30	

Experiment No. 8.

Scheele's original receipt is very nearly one part by weight of arsenic to three each of copper sulphate and potassium carbonate, and is frequently so given. The proportions as given by Scheele are, eleven ounces of the first, and thirty-two of each of the others. In molecules, supposing the potassium carbonate to be pure and anhydrous, as he directs it should be, the receipt will be as follows:—

As_2O_3 ,	1.
CuO ,	2.32
K_2CO_3 ,	4.34

Or nearly double the amount of potassium carbonate required in the reaction, —



A portion was, therefore prepared, using

	Parts.	Molecules.
Copper sulphate	6	2.35
Potassium carbonate,	3	2.17
Arsenic trioxide,	2	1.

The filtrate was slightly acid and blue, but the potassium carbonate used not quite anhydrous. The color produced was fully equal to that produced by the ordinary receipt. The filtrate contained arsenic.

ANALYSIS No. XIV.

	Per cents.	Atomic Ratios.
Copper oxide,	51.37	6.62
Arsenic trioxide,	39.94	2.02
Sulphur trioxide,	1.80	.22
Water,	6.61	3.67

This is an almost exact mixture of tribasic sulphate and arsenite. It dissolved in ammonia with a blue color, and did not blacken on boiling. The potassium carbonate may, therefore, be considerably diminished from that called for in Scheele's receipt.

Experiment No. 9.

This was nearly a repetition of Experiment No. 4 as to quantities used. The object being in this case to study more fully the effects of washing, the proportions taken approximate closely to Scheele's receipt:—

	Parts.	Molecules.
Copper sulphate,	3	2.35
Arsenic trioxide,	1	1.
Potassic carbonate,	3	4.34

The solutions were mixed and boiled for half an hour; the first (No. XV.) was washed until the wash-water was free from sulphates; the other (No. XVI.) until the wash-water was free from arsenic.

ANALYSIS No. XV.

	Per cents.	Atomic Ratios.
Copper oxide,	52.23	6.60
Arsenic trioxide,	35.41	1.79
Sulphur trioxide,	5.88	.74
Water,	6.02	3.35
	<hr/> 99.54	

ANALYSIS No. XVI.

	Per cents.	Atomic Ratios.
Copper oxide,	57.18	7.20
Arsenic trioxide,	25.62	1.30
Sulphur trioxide,	6.31	.79
Water,	10.85	3.90

Experiment No. 10.

This preparation was made exactly according to Scheele's own directions, as given by himself in the Proceedings of the Stockholm Academy, using the English translation for the weights and measures. The sample was divided after precipitation. No. XVII. was washed by decantation with the amount of water he specifies.

No. XVIII. was first boiled with water, and then washed with hot water so long as arsenic was found in the filtrate. The proportions used were,—

	Parts.
Arsenic trioxide,	11
Potassium carbonate,	32

Dissolved the potassium carbonate in thirty-two parts of water, added the arsenic trioxide boiled and filtered.

	Parts.
Copper sulphate crystallized,	32
Water,	192

Dissolved and boiled while hot; added, with constant stirring, the hot solution of arsenic trioxide.

ANALYSIS No. XVII.

	Per cents.	Atomic Ratios.	
		Found.	Taken.
Copper oxide,	50.76	3.10	2.32
Arsenic trioxide,	40.82	1.00	1.
Sulphur trioxide,	1.63	.10	
Water,	6.41	1.75	
	<hr/> 99.62		

ANALYSIS No. XVIII.

	Per cents.	Atomic Ratios.
Copper oxide,	49.25	6.20
Arsenic trioxide,	42.66	2.15
Sulphur trioxide,	.42	.05
Water,	6.71	3.72
	<hr/> 99.04	

In summing up, I will first call attention to the fact that in no one of the eighteen samples does the arsenic exist in these compounds in as great a ratio as required by Bloxam's formula. Further, they all contain water, and this water is not driven off at a temperature of 150° C. In every case, arsenic was found in the filtrate, sometimes in considerable amount, as is shown by comparison of the ratios of copper sulphate and arsenic trioxide taken, and the ratios between the copper oxide and arsenic, as found in the analysis. All the samples dissolved in ammonia with a blue color.

In Experiments Nos. 4, 9, and 10 almost identical amounts of substances were taken; but the results, as will be seen, differ widely.

Scheele's green may, according to my experiments, be described as a

more, or less basic copper arsenite, which may or may not contain basic copper sulphate and carbonate; the composition of it seeming to depend to a considerable extent upon the degree of concentration of the liquid from which it is precipitated. Its basicity also seems to depend to a considerable extent upon the same fact, the more dilute the solution the more basic the salt.

The composition also depends, to some extent, on the amount of wash-water used in washing it.

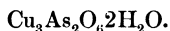
The normal pigment which is represented by Analysis XVIII. may be described as follows:—

It is of a yellowish green color, soluble in dilute acids and in caustic alkalis. It dissolves in alkalis with a blue color, and is decomposed by excess of soda or potassa, or their carbonates, but is not decomposed by ammonia, even upon boiling. It does not blacken upon boiling with distilled water. When dissolved in ammonia, if a solution of soda or potash is added, the solution is bleached, from the reduction of the copper salt to a cuprous salt.

Its average composition, as generally prepared, omitting the sulphur trioxide which is generally found in it, is about as follows:—

Copper oxide,	50.00
Arsenic trioxide,	42.00
Water,	8.00

This approximates closely to the formula,



This formula would give the following percentages:—

Copper oxide,	51.44
Arsenic trioxide,	41.93
Water,	7.93

Taking this view of the subject, Scheele's green is the normal tri-cupric arsenite, and corresponds to the triargentate arsenite described by Bloxam.

It is almost impossible, however, to obtain a perfectly constant product, from the strong tendency to form basic sulphates and basic arsenites.

As a matter of economy in the preparation, it will be found more advantageous to take the following proportions rather than those given by Scheele:—

	Parts.
Copper sulphate,	6
Arsenic trioxide,	2
Sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$,	8

Dissolve the soda and arsenic in ten parts of water, and the copper sulphate in forty parts of water; filter both solutions if necessary. Mix while boiling, boil for a few minutes, and then allow to stand until next day; pour off the supernatant liquid, fill up the vessel with hot water; repeat this operation about three times, then filter, and dry at about 100°C .

In analyzing these salts, the water was determined by ignition in a current of oxygen. The water being collected and weighed in a chloride of calcium tube. The arsenic was determined in various ways, but it was found that the conversion into arsenic pentoxide and trituration with uranium solution gave the most satisfactory results. The copper was determined with the battery.

The separation of copper and arsenic was made either by boiling with a slight excess of potassa with previous oxidation by nitric acid or bromine, or by adding potassa, and then passing hydrogen sulphide through the solution until the copper was completely precipitated.

My thanks are due to my assistant, E. R. Hills, for the able manner in which he has aided me by making many analyses of these salts, — an undertaking that can be appreciated only by those who have tried working with copper and arsenic in combination.

Since the above paper was finished, I have succeeded in obtaining two samples of copper arsenite as found in commerce. The first of these resembled closely that analyzed in Analysis No. XII. in color, and on examination it was found to contain carbon dioxide and sulphur trioxide; the other resembled Analysis No. XVIII., and, like it, contained a trace of sulphate.

Boston, June 1st.